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AFRL-SR-BL-TR-02-

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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 15 Feb 02		3. REPORT TYPE AND DATES COVERED Final Report 01 Apr 00 - 31 Mar 01	
4. TITLE AND SUBTITLE THEORETICAL SIMULATIONS OF WEAKLY BOUND CLUSTERS OF LIGHT ATOMS AND SMALL MOLECULES				5. FUNDING NUMBERS F49620-00-1-0202  2312/CV  61102F	
6. AUTHOR(S) Professor Millard H. Alexander					
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Chemistry and Biochemistry University of Maryland College Park, MD 20742-2021				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) AFOSR/NL 801 N. Randolph Street, Suite 732 Arlington VA 22203-1977				10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES					
12a. DISTRIBUTION AVAILABILITY STATEMENT				12b. DISTRIBUTION CODE	
				<p>AIR FORCE OFFICE OF SCIENTIFIC RESEARCH/AFOSR</p> <p>NOTICE OF TRANSMITTAL</p> <p>HAS BEEN REVIEWED AND IS APPROVED FOR PUBLIC RELEASE</p> <p>LAW AFR 190-12. DISTRIBUTION IS UNLIMITED.</p>	
13. ABSTRACT (Maximum 200 words) This instrumentation grant supported the purchases of two multiprocessor, high-speed UNIX workstations (an HP J5600 and an IBM RS6000/44P). These computer system were (and continue to be) employed in the theoretical study of the interactions of boron and aluminum atoms with molecular hydrogen. Quantum chemical calculations of the relevant potential energy surfaces were carried out. With these potential energy surfaces, the energetics, structure, and nuclear dynamics of the weakly bound clusters was investigated, in particular with fully-quantum determination of the bound state energies and wavefunctions of the binary complex and with path-integral, quantum molecular dynamics simulations of more extended systems.					
14. SUBJECT TERMS				15. NUMBER OF PAGES	
				16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT		18. SECURITY CLASSIFICATION OF THIS PAGE		19. SECURITY CLASSIFICATION OF ABSTRACT	
				20. LIMITATION OF ABSTRACT	

20020305 108

**THEORETICAL SIMULATIONS OF WEAKLY BOUND CLUSTERS  
OF LIGHT ATOMS AND SMALL MOLECULES**

FINAL REPORT

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Air Force Office of Scientific Research

Grant Number F49620-00-1-0202

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## I. SUMMARY OF WORK AND DESCRIPTION OF WORK ACCOMPLISHED

This instrumentation grant supported the purchase of two multiprocessor, high-speed UNIX workstations (an HP J5600 and an IBM RS6000/44P). These computer system were (and continue to be) employed in the theoretical study of the interactions of boron and aluminum atoms with molecular hydrogen. An understanding of these interactions is of great importance for the ultimate development of novel propellants based on the doping of light atoms into cryogenic hydrogen. Quantum chemical calculations of the relevant potential energy surfaces were carried out. With these potential energy surfaces, the energetics, structure, and nuclear dynamics of the weakly bound clusters was investigated, in particular with fully-quantum determination of the bound state energies and wavefunctions of the binary complex and with path-integral, quantum molecular dynamics simulations of more extended systems.

Our AFOSR funded research project involves close collaboration with the experimental group of Dagdigian at The Johns Hopkins University. They have used optical spectroscopy to characterize experimentally the non-bonding interactions of the aluminum atom, in both its ground and excited electronic states, with molecular hydrogen.<sup>1,2</sup> Recently, several excited electronic transitions in the binary Al-H<sub>2</sub> complex were observed and characterized.<sup>3</sup> The rotational structure of several bands were resolved and assigned, and the average Al-H<sub>2</sub> separation in the ground vibronic level was determined in order to provide direct information on the length scale of the Al-H<sub>2</sub> interaction. Using ground-state combination differences and employing optical-optical double resonance spectroscopy, Dagdigian and Tan were able to determine the rotational constant  $B$  and parity doubling parameter  $p$  for the ground bend-stretch levels of Al(3p)-oH<sub>2</sub> and Al(3p)-pD<sub>2</sub>. These are the most strongly bound nuclear spin modifications of the complexes.<sup>4</sup>

To understand and interpret these experiments, we used fully quantum calculations of the ground states of these binary complexes. Two sets of potential energy surfaces were employed: those computed earlier Williams and Alexander,<sup>4</sup> for which the H-H bond distance  $r$  was fixed at the diatomic equilibrium separation, and those

determined by new calculations in which the dependence on  $r$  was included.<sup>3</sup> These *ab initio* calculations were carried out with the MOLPRO 2000 program suite,<sup>5</sup> installed on our new Unix workstations. The determination of the bound states was done with our Hibridon 4.1 program suite,<sup>6</sup> developed partially with AFOSR support.

The agreement of the experimental values of the parameters and those calculated on the basis of PESs with the  $r$  dependence included is excellent, considerably improved over the values determined from the fixed- $r$  PESs.<sup>3</sup> In addition, the dissociation energy of the complex computed with the fixed- $r$  PESs is  $\sim 15\%$  smaller than the value computed with the full PESs. In the Al-H<sub>2</sub> complex, which has a  $T$ -shaped equilibrium geometry, the increased attraction in the expansion phase of the H<sub>2</sub> vibration more than compensates for the reduced attraction in the compression phase. One conclusion of this comparison is that, for weakly bound complexes of atoms with molecular hydrogen, it is necessary to take into account the dependence of the PESs on the H<sub>2</sub> bond distance.

In a collaborative project with Soonmin Jang and Greg Voth at the University of Utah, we incorporated our B-H<sub>2</sub> PESs into their path-integral Monte-Carlo simulations of the diffusion and recombination of B impurities in solid  $p$ H<sub>2</sub>. This PES, which incorporates the dependence of the interaction potential on the orientation of the  $2p$  electron, was based on the *ab initio* calculations of Williams and Alexander,<sup>4</sup> is a considerable improvement over the simplified potential, obtained by averaging over all directions of the B  $2p$  orbital, which was used in the earlier work of Jang, Jang, and Voth.<sup>7</sup>

We found that the inherent anisotropy of the hexagonal close-packed lattice is significant enough to warrant the use of electronic-orientation-dependent potentials whenever possible; the average B-H<sub>2</sub> attractive potential energy is lowered by nearly 20% when this is included. When additional anisotropy is introduced by the presence of a site vacancy, the importance of the orientation-dependent potential is further evidenced by the behavior of the B- $p$ H<sub>2</sub> pair correlation functions. The orientation-dependent potential introduces additional flexibility, which allows the electronic and spatial coordinates of the B to adapt to the presence of an adjacent vacancy.

Similar simulations for embedded Al impurities in solid H<sub>2</sub> are now underway , based on our latest Al-H<sub>2</sub> PESs.<sup>3</sup> As described earlier in this report, these PESs include an averaging over the vibrational motion of the H<sub>2</sub> moiety, and are considerably more accurate than the earlier PESs of Williams and Alexander,<sup>4</sup> which were determined for a rigid H<sub>2</sub> distance.

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5. MOLPRO is a package of *ab initio* programs written by H.-J. Werner and P. J. Knowles, with contributions from R. D. Amos, A. Bernhardsson, A. Berning, P. Celani, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, C. Hampel, G. Hetzer, T. Korona, R. Lindh, A. W. Lloyd, S. J. McNicholas, F. R. Manby, W. Meyer, M. E. Mura, A. Nicklass, P. Palmieri, R. Pitzer, G. Rauhut, M. Schütz, H. Stoll, A. J. Stone, R. Tarroni, and T. Thorsteinsson.
6. HIBRIDON is a package of programs for the time-independent quantum treatment of inelastic collisions and photodissociation written by M. H. Alexander, D. E. Manolopoulos, H.-J. Werner, and B. Follmeg, with contributions by P. F. Vohralik, D. Lemoine, G. Corey, B. Johnson, T. Orlikowski, W. Kearney, A. Berning, A. Degli-Esposti, C. Rist, and P. Dagdigan.
7. S. Jang, S. Jang, and G. A. Voth, J. Phys. Chem. **103**, 9512 (1999).

### III. LIST OF PUBLICATIONS PREPARED UNDER AFOSR GRANT NO. F49620-00-1-0202

1. J. R. Krumrine, M. H. Alexander, X. Yang, and P. J. Dagdigian, "Experimental and theoretical study of the electronic spectrum of the  $\text{BAr}_2$  complex: Transition to the excited valence  $\text{B}(2s2p^2\ ^2D)$  state," J. Chem. Phys. **112**, 5037 (2000).
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3. J. R. Krumrine, S. Jang, M. H. Alexander, and G. A. Voth, "Quantum molecular dynamics and spectral simulation of a boron impurity in solid *para*-hydrogen," J. Chem. Phys. **113**, 9079 (2000).
4. X. Tan, P. J. Dagdigian, J. Williams, and M. H. Alexander, "Experimental and theoretical investigation of the rotational structure of the  $\text{Al-H}_2/\text{D}_2$  complex," J. Chem. Phys. **114**, 8938 (2001).

### IV. LIST OF PARTICIPATING SCIENTIFIC PERSONNEL

Millard Alexander, Principal Investigator, Distinguished University Professor.

Jason Williams, Postdoctoral Research Fellow (Ph. D. University of California, Irvine, 1998)

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